Energy Tutorial: Synthetic Fuels 101

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The goal for today

To discuss unconventional, emerging technologies that could produce fuels in a renewable, sustainable manner.

Our definition of “Synthetic Fuels” for today’s purpose.

Some previous GCEP Energy 101 Tutorials that are complementary to the material presented today:

• Solar Energy 101 Prof. Nathan Lewis
• Solar Cells 101 Prof. Michael McGehee
• Electrocatalysis 101 Prof. Thomas F. Jaramillo
Outline

• Fossil fuels
• Pathways to renewable, synthetic fuels
• Overview of thermodynamics & efficiency
• Electrochemical & Photo-electrochemical pathways
  – Hydrogen fuels
    • Lab-based devices
    • Techno-economics of large-scale facilities
    • Chemical & physical factors at play → modeling efficiency
  – Extending to carbon-based fuels
• Summary
Total primary energy supply: The facts

- Today: 17 TW of power.
- 80% comes from fossil fuels (oil, coal, natural gas).

Fossil fuels: An amazing resource

- Consider petroleum/gasoline
  - Massive world-wide resource, extremely abundant
    - Provides ~ 5 TW of power across the globe (out of 17 TW total)
  - Huge energy density
    - Can drive a car 500 miles on one tank of gas, or fly a commercial jet half-way around the earth.
    - A full tank of gasoline in a car is approximately equivalent to:
      - The potential energy of 1 million gallons of water at 200 ft elevation
      - The electrical energy stored in 80,000 iPhone 6 batteries
  - High power density
    - Can power anything… automobiles, trucks, shipping vessels, commercial and military aircraft….
    - The power transfer in filling up your car at the pump is approximately 5 MW.
  - Yet very chemically stable
    - When you drive your car, do you worry about it exploding?
  - Easy to store and to transport
    - Approx. 100,000 miles of gasoline pipeline in the USA.
    - As a liquid fuel it can fit into any size and shape of container with ease.
  - Cost
    - How do the ‘high’ gas prices of today (~ $3-$4/gallon) compare with other consumer goods? Bottled water? Milk? Orange juice?
  - Convenience
    - Have you ever timed yourself at the gas pump? How long does it take to fill the tank?

No wonder why we consume so much petroleum! This is also why fossil fuels are so hard to beat….
Gasoline and related hydrocarbons

<table>
<thead>
<tr>
<th># of carbon atoms</th>
<th>100-10,000</th>
<th>15-25</th>
<th>7-18</th>
<th>5-9</th>
<th>1-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavier</td>
<td></td>
<td></td>
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</tr>
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</table>

- Plastic
- Motor Oil
- Diesel
- Gasoline
- Methane
- Propane
- Ethane
- Butane
Petroleum Refining

Figure 1.1 Refinery for converting crude oil into a variety of marketable products.

Recommended viewing:
The History Channel “Modern Marvels” series
- “Gasoline” (2002)
- “Secrets of Oil” (2008)
A “conventional” approach to synthetic fuels

Courtesy: Sasol
Energy Density

![Graph showing energy density comparison between various fuels and energy storage methods. The graph plots volumetric energy density against gravimetric energy density. Key points include Diesel, Gasoline, Ethanol, Coal, Methanol, Batteries, Liquid H₂, and 150 bar H₂.]
The broad vision: Renewable production of fuels and chemicals

Option #1: Fuels

Option #2: Chemical Products

Option #3: Chemical Precursors

- Hydrogen (H₂)
- Carbon monoxide (CO)
- Methanol (CH₃OH)
- Ethanol (C₂H₅OH)
- Butanol (C₄H₉OH)
- Methane (CH₄)
- Ethylene (C₂H₄)
- Gasoline (C₅-C₉)
- Diesel (C₇-C₁₅)
- Others...
Many possible schemes for solar fuels

**Photobiologic** → engineered organisms that synthesize fuels

**Photochemical** → metallorganic absorbers and redox mediators

**Solar thermal** → heterogeneous catalysis.

11 MW near Seville

**Solar electricity** → electrocatalysis
(Photo-)Electrochemical Pathways

Scheme 1: Separate devices for electricity generation and for fuel production.

Scheme 2: One integrated device for solar harvesting and fuel production.
Thermodynamic considerations for (photo-)electrochemical conversions related to energy


<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product</th>
<th>$E^0$ vs. RHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2H⁺ + 2e⁻</td>
<td>H₂</td>
<td>0.00 V</td>
</tr>
<tr>
<td>CO₂ + 2H⁺ + 2e⁻</td>
<td>CO + H₂O</td>
<td>-0.11 V</td>
</tr>
<tr>
<td>CO₂ + 6H⁺ + 6e⁻</td>
<td>CH₃OH + H₂O</td>
<td>+0.02 V</td>
</tr>
<tr>
<td>CO₂ + 8H⁺ + 8e⁻</td>
<td>CH₄ + 2H₂O</td>
<td>+0.16 V</td>
</tr>
<tr>
<td>2CO₂ + 12H⁺ + 12e⁻</td>
<td>C₂H₄ + 4H₂O</td>
<td>+0.07 V</td>
</tr>
<tr>
<td>2CO₂ + 12H⁺ + 12e⁻</td>
<td>C₂H₅OH + 3H₂O</td>
<td>+0.08 V</td>
</tr>
<tr>
<td>3CO₂ + 18H⁺ + 18e⁻</td>
<td>C₃H₇OH + 5H₂O</td>
<td>+0.09 V</td>
</tr>
<tr>
<td>O₂ + 4H⁺ + 4e⁻</td>
<td>2H₂O</td>
<td>+1.23 V</td>
</tr>
</tbody>
</table>

All values are close to the H₂ evolution potential (0.00 V).

Cathode: “Fuel synthesis” Reactions

Anode: The “Balancing” Reaction

E (V vs. RHE)

E°ₜ₉/₅₂₀

i (mA/cm²)
Calculating STF Efficiency

**Power Efficiency:**
\[
\frac{\text{Power Out}}{\text{Power In}} = \frac{\text{Rate of chemical energy production}}{\text{Power input from solar energy}} = \left[ \sum _i \left( \frac{\text{mmol fuel}_i}{\text{second}} \right) \left( \frac{\Delta G_i}{\text{mol}} \right) \right] \left[ \frac{\text{mA/cm}^2}{\text{mol}} \right] \left( \frac{\text{cm}^2}{\text{mA/cm}^2} \right) \left( \frac{\text{Area cm}^2}{\text{cm}^2} \right)
\]

- Summed over all fuels
- Rate at which each fuel is produced
- Chemical energy within each fuel

E.g. AM1.5 solar radiation (100 mW/cm²)

Alternatively one can express fuel production rate in mA/cm² and \( \Delta G \) as a cell potential (V):
\[
\frac{\text{Power Out}}{\text{Power In}} = \frac{\text{Rate of chemical energy production}}{\text{Power input from solar energy}} = \left[ \sum _i \left( \frac{\text{mA fuel}_i}{\text{cm}^2} \right) \left( \Delta G_i \right) \left( \frac{\text{V}}{\text{mol}} \right) \right] \left[ \frac{(\text{P total mW/cm}^2)}{(\text{cm}^2)} \right]
\]

- Insolated area of the device

GLOBAL CLIMATE AND ENERGY PROJECT | STANFORD UNIVERSITY
Example: Solar-to-hydrogen (STH) Efficiency

Power Efficiency:

\[
\frac{\text{Power Out}}{\text{Power In}} = \frac{\text{Rate of chemical energy production}}{\text{Power input from solar energy}} = \left[ \frac{(\text{mmol} \ H_2 \ \text{second})}{(237,000 \ J \ \text{mol})} \right] \left[ \frac{\left( \sum_i \frac{(\text{mA} \ H_2)}{\text{cm}^2} \right)(1.23 \ V)}{(P_{\text{total} \ \text{cm}^2})} \right]
\]

Summed over all fuels  
Rate at which each fuel is produced  
chemical energy within each fuel

e.g. AM1.5 solar radiation  
(100 mW/cm²)  
Insolated area of the device

Alternatively one can express fuel production rate in mA/cm² and ΔG as a cell potential (V):

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\]

Assumes 100% of current goes to water-splitting
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• Summary
Hydrogen (H₂)
Conventional H₂ production

Fossil-fuel powered Electrolysis
~$4-$5 / kg

Steam Methane Reforming/
Coal Gasification
~$1 / kg

ExxonMobil Baton Rouge, LA
http://www.exxonmobilbr.com/

Annually
~65 billion kg (2007)
~$100 billion
2-3% Global Energy Consumption

Ammonia Synthesis

Crude Oil Refining

State of Fuel Cell cars today (Oct 2014)

• Test fleets from many major automakers
  – > 3M mi. driven
  – > 27k refuelings
• Toyota FCV, first car to go on sale in 2015
  – MSRP ~$65k

Fuel Cell Electric Vehicles are breaking into the market, but cost must come down for mass adoption.

California Fuel Cell Partnership
NREL
Noteworthy devices for Photoelectrochemical (PEC) H₂ production

**AlGaAs/Si**
- Technion Univ.
- Nagoya Inst.
- Hahn-Meitner Inst.
- **18.3 % STH**

**GaAs/p-GaInP₂**
- NREL
- **12.4 % STH**

**3jn-CIGS**
- Uppsala University (Sweden)
- **10 % STH**
Solar photoelectrochemical (PEC) $\text{H}_2$ production

Video courtesy of Dr. Todd Deutsch, NREL
Techno-economics

*How much might H$_2$ cost if produced by large-scale solar PEC water-splitting?*
How to conduct a techno-economic analysis

- Define PEC material and performance ranges
- Brainstorm PEC device and/or reactor types
- Downselect PEC reactor on the basis of cost and performance

- Develop bill of materials (BOM) and capital costs
- Design auxiliary systems and conceptual plant (used modular approach)

- Calculate levelized H₂ cost using H2A spreadsheet
- Perform sensitivity analysis

Chemical engineering plant design

Reactor Type 1: Colloidal Suspension

Type 1: Single Bed
Particle Suspension
STH Efficiency 10%

Reactor Type 2: Dual-bed Colloidal Suspension

Type 2: Dual Bed
Particle Suspension
STH Efficiency 5%

Reactor Type 3: Fixed Panel PEC Array

**Type 3: Fixed Panel Array**

STH Efficiency 10%

**Type 3: Fixed Panel Array**

Plant Area 219,149 m²

Reactor Type 4: Tracking Concentrator Array

Type 4: Tracking Concentrator Array
STH Efficiency 15%

Technoeconomics of Photoelectrochemical H₂

- **Particle systems:** Low cost but low demonstrated performance.
  - **$1.60/kg H₂**
  - **$3.20/kg H₂**
  - **$10.40/kg H₂**
  - **$4.00/kg H₂**

- **Panel systems:** Higher demonstrated bench-scale efficiencies but higher cost.
  - **Target:** $2 – $4/gge
Sensitivity Analysis: Efficiency is the cost-driver

![Graph showing cost sensitivity analysis for different parameters: Base Case, Efficiency, PEC Cell Cost, and Lifetime. The graph indicates that the cost driver is efficiency with values of $2.90, $3.70, and $3.90 for different cases.]

Band structure of a photoelectrode

Bandgap ($E_g$)

Band edge alignment

Surface catalysis

Stability
Maximum STH efficiency vs. bandgap (single-absorber)

Developing materials with appropriate bandgaps is a critical challenge...
But exactly what bandgaps should one target?

Modeling STH efficiencies

Modeling ‘Realistic’ PEC efficiencies

Device Options

Solid-state $V_{oc}$
- High $V_{oc}$
  ($\sim$470mV loss)
- Low $V_{oc}$
  ($\sim$590mV loss)

Catalyst Activity
- Precious metal
  (Pt/Ru)
- Non-precious metal
  (MoS$_2$/MnO$_x$)

Shunt
- Zero shunt losses
  ($R_{sh} = \infty \, \Omega$)
- “Significant” shunt losses
  ($R_{sh} = 100 \, \Omega$)

Absorber Configuration
- Single
- Dual stacked
- Dual side-by-side

Calculated theoretical limits for a ‘realistic’ STH efficiency as a function of bandgap, taking into account:

- Reaction overpotentials ($H_2$ and $O_2$)
- Entropic losses ($V_{ph} < E_g$)
- Shunts

Can reach 10-11% STH with $E_g \sim 2.3$ eV

Calculated theoretical limits for a ‘realistic’ STH efficiency as a function of bandgap, taking into account:
• Reaction overpotentials (H₂ and O₂)
• Entropic losses (V_{ph} < E_g)
• Shunts

Multi-junction devices

\[
\begin{align*}
2H_2O & \rightarrow 2H_2 + O_2 \\
4H^+ + 4e^- & \rightarrow 2H_2 \\
\Delta E^0 & = 1.23 V
\end{align*}
\]
Tandem devices

Ohmic contact
Semiconductor photoanode

Band gap \( E_G \)

\( 4H^* + 4e^- \rightarrow 2H_2 \)

\( 2H_2O + 4h^* \rightarrow O_2 + 4H^* \)

Overall:
\( 2H_2O \rightarrow O_2 + 2H_2 \)

Semiconductor photocathode

Ohmic contact

1.23 eV
Multi-junction or Tandem Devices

Calculated theoretical limits for a ‘realistic’ STH efficiency as a function of bandgap, taking into account:

- Reaction overpotentials \( (H_2 \text{ and } O_2) \)
- Voltage losses \( (V_{ph} < E_g) \)
- Shunts

Can reach 23 % STH with \( E_{g1} \sim 1.2 \text{ eV} \) & \( E_{g2} \sim 1.8 \text{ eV} \)

A vision of a solar fuels device

Many high-performance materials are needed to make this work!

www.solarfuelshub.org
The Joint Center for Artificial Photosynthesis (JCAP)
Three primary figures of merit for catalysts

Q: Which of these is most critically needed in catalyst development?

A: It depends on the reaction!
Summary of Electrocatalyst Development

• The hydrogen evolution reaction (HER)
  – Precious metals (e.g. Pt) reach all the important performance metrics.
  – Non-precious metals are not quite as active as Pt, but they might still be feasible.
    • Some are only stable in near-neutral or base (e.g. NiMo).
    • Some are only stable in acid (e.g. metal phosphides or sulfides, e.g. MoS$_2$).
  – Selectivity for H$_2$ is excellent for all of these catalysts.

• The oxygen evolution reaction (OER)
  – Lots of room for improvement in activity, even for the best precious-metal based systems (e.g. IrO$_2$, RuO$_2$). Some non-precious-metal catalysts are as good or better, but only stable in near-neutral or alkaline conditions (e.g. FeNiO$_x$).
  – Theory has explained why achieving desired activity is so challenging.
  – Dimensionally stable anodes (DSAs) are extremely stable, proven in industrial electrolysis.
  – Selectivity is generally only a concern for seawater electrolysis, where Cl$_2$ and Br$_2$ evolution are often favored over O$_2$ evolution.

• The CO$_2$ electro-reduction reaction to fuels and chemicals
  – The most challenging of the three reactions, by far. There is a lack of viable candidate catalysts.
  – Producing 2-electron products such as formate or CO is much easier than more reduced products such as hydrocarbons or alcohols.
  – Copper produces an large fraction of hydrocarbons and alcohols, though selectivity is poor for any one product and high overpotentials are needed.
  – Much work needed to make these processes feasible.
Benchmarking H₂ and O₂ catalysts at JCAP


Benchmarking $\text{H}_2$ and $\text{O}_2$ catalysts at JCAP

Thermodynamics & Kinetics of CO$_2$ reduction


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All values are close to the $H_2$ evolution potential (0.00 V).

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Copper catalysts

- CO and formate pull near constant current across voltage range.

- H₂ is mostly constant, then increases at high V.

- CH₄ production rate constantly increasing with Tafel behavior.

- C₂ and C₃ products clearly rise and fall together.

Synthetic Fuels: Take-home messages

• Chemical fuels are a magnificent form of energy storage.
• Researchers in the area of solar fuels aim to develop a way to produce fossil fuel-like molecules from water, CO₂, and solar energy.
• Technologically, this can already be done. However, better catalysts and semiconductors need to be developed if the process is to ever become cost-competitive with fossil fuels.
• A techno-economic analysis for the case of H₂ shows that it is possible to reach that goal if materials with appropriate properties can be developed.
• This is incentive to strengthen our efforts in R&D in this field, keeping our eyes on commercial possibilities as improved materials are developed.